Effect of combinational doping on x-ray sensitivity of a-Se films

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Received 29 January 1998

Abstract. The x-ray sensitivity of a-Se films (\sim 130 μ m) as a function of combinational doping, i.e. chlorine (\sim 5 to 40 ppm) and arsenic (\sim 0.15 to 0.35%, by weight) has been studied using the potential decay technique. The films doped combinationally with \sim 30 ppm chlorine and \sim 0.30% arsenic show the maximum sensitivity. This has been attributed to the optimum combinational and complementary roles played by the two dopants, i.e. the mobility enhancement role of chlorine and charge sustaining role of arsenic.

1. Introduction

Chemically modified amorphous selenium (a-Se), i.e. doped with suitable dopants such as chlorine and arsenic, finds applications [1,2] as an x-ray imaging material in xeroradiography (XR) photoreceptors. One of the problems in these photoreceptors is their inadequate x-ray sensitivity which limits the use of XR to specialized applications like mammography rather than in general radiological applications such as bone extremities, etc. To enhance the x-ray sensitivity, designated as S, in a-Se, it is essential to understand the physics of these photoreceptor films at a microscopic level. For this, many fundamental investigations have already been made [3-8] to study various important parameters such as defect states, mobility of charge carriers, effect of dopants and so on related to the S of a-Se films. However, S in a-Se films can most easily be understood in terms of charge generation energy (ξ) required per pair, i.e. the x-ray energy required in eV to generate an electron-hole pair in a-Se as defined by Donovan [1]. But, surprisingly, detailed investigations are lacking in the literature on the above important aspect and only a few results are reported [1] on the calculation of ξ in a-Se. As per these investigations [1] the minimum value of ξ in a-Se films doped combinationally with ~10 and 20 ppm chlorine and 0.35% arsenic has been found to be \sim 30-40 eV per pair. Keeping the above in mind we have made, for the first time, the much needed systematic investigations to study the effect of combinational doping, i.e. with chlorine and arsenic, on the x-ray sensitivity of a-Se using the potential decay technique. The sensitivity parameters S and ξ have been found to depend strongly on combinational doping concentrations and these important and interesting results are reported in this short communication.

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2. Experimental details

Thick films (\sim 130 μ m) of selenium doped with chlorine (\sim 5 to 40 ppm) and arsenic (\sim 0.15 to 0.35% by weight) were vacuum deposited, as described earlier [5], on an ultrasonically cleaned aluminium substrate. The area of the sample was \sim 100 cm². The potential decay technique was used to calculate the values of S and ξ . In this technique the samples are charged positively to some initial potential V_I using the well known corona discharge technique and then they are exposed to x-rays at 50 kV (1 mm Al filtration) and the residual potential V_R , i.e. the potential left after exposure was measured using an experimental set-up comprising a dark chamber, x-ray unit and a Keithley 610C electrometer coupled to Riken Denshi F43P X-Y-T recorder. The exposure rate was measured using a Keithley model 35065 dosimeter.

3. Results and discussion

Measurements were performed in a variety of samples containing chlorine in the range of 5 to 40 ppm and arsenic in the range 0.15% to 0.35% but only two curves for two typical cases (curves for other cases being similar in nature) of potential decay are shown in figure 1. The two typical cases in figure 1 correspond to a minimally sensitive case, i.e. the pure a-Se films (curve A) and maximally sensitive case (curve B), i.e. optimum combinationally doped a-Se having ~30 ppm chlorine and ~0.30% arsenic. It is important to mention here that, although the potential accepted by the samples remains fairly constant in the dark, in order to take into account even a small dark decay the value of the potential existing at the time of x-ray irradiation has been used for calculating the values of S and ξ . Similar values of V_I and V_R for other combinationally doped cases are given in table 1.

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Table 1. X-ray sensitivity parameters of a-Se film	Table 1.	X-rav	sensitivity	parameters	of	a-Se	films
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Sample	Doping levels in selenium	V, (V)	V _R (V)	S (R ⁻¹)	ξ (eV per pair)
no	Seleman	(٧)	(•)		(ev per pair)
1	No doping	1350	1040	6.3	43.0
2	5 ppm, 0.30%	1350	955	8.5	34.5
3	10 ppm, 0.30%	1350	890	10.0	29.0
4	15 ppm, 0.30%	1350	820	12.0	25.5
5	20 ppm, 0.30%	1350	760	13.9	23.0
6	25 ppm, 0.30%	1350	720	15.1	21.5
7	30 ppm, 0.30%	1350	710	15.5	21.0
8	35 ppm, 0.30%	1350	720	15.1	21.5
9	40 ppm, 0.30%	1350	740	14.5	22.0
10	0.15%, 30 ppm	1350	900	9.8	30.0
11	0.20%, 30 ppm	1350	760	12.0	25.5
12	0.25%, 30 ppm	1350	740	14.5	22.0
13	0.30%, 30 ppm	1350	710	15.5	21.0
14	0.35%, 30 ppm	1350	740	14.5	22.0

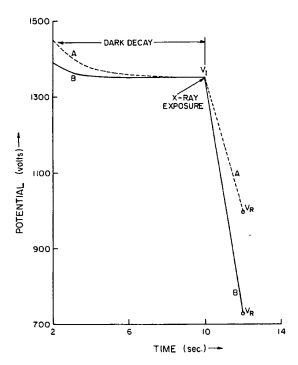


Figure 1. Potential decay characteristics of pure (curve A) and optimum combinationally doped (curve B) a-Se films.

The values of S and ξ were calculated using equations given by Boag [9] and Donovan [1] respectively, i.e.

$$S = \frac{1}{0.693E} (\log V_I - \log V_R) \tag{1}$$

and

$$\xi = \frac{IEAB}{n} \tag{2}$$

where E is the rate of exposure, V_I is the initial existing potential at the time of exposure, V_R is the residual potential after exposure, I is the incident energy, A is the area of the sample, B is the percentage of absorption, n = CV/e is the rate of generation of free carriers per

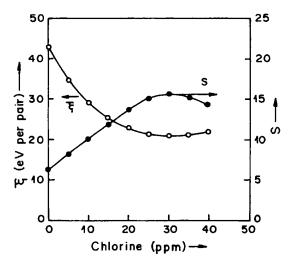


Figure 2. Plot of S and ξ as a function of chlorine concentration for fixed arsenic concentration of \sim 0.30% by weight.

second, C is the gometrical capacitance, $V = V_I - V_R$ and e is the electronic charge. In the present case V_I and V_R are taken from table 1. The values [1] of I being $\sim 2.12 \times 10^{14}$ eV cm⁻² R⁻¹ and $B \sim 64\%$. The measured exposure rate, E, being $\sim 26 \times 10^{-3}$ R s⁻¹ and $A \sim 100$ cm². Putting the values of various parameters into equations (1) and (2) the values of S and S for different combinationally doped a-Se cases have been obtained at a fixed field $\sim 1 \times 10^7$ V m⁻¹ and are shown in table 1.

The data in table 1 have been plotted in figures 2 and 3. Figure 2 shows the plot of S and ξ as a function of chlorine concentration at a fixed arsenic concentration of 0.30% by weight. Similarly, figure 3 shows the plot of S and ξ as a function of arsenic concentration for fixed chlorine concentration of \sim 30 ppm. It is seen from these figures that the value of S and ξ increase and decrease respectively on combinational doping from the values of 6.3 R^{-1} and 43 eV per pair in the pure a-Se case to a respective maximum and minimum of 15.5 R^{-1} and 21 eV

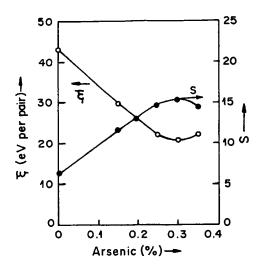


Figure 3. Plot of S and ξ as a function of arsenic concentration for a fixed chlorine concentration of $\sim \!\! 30$ ppm.

per pair respectively, in an optimum combinationally doped case, i.e. ~30 ppm chlorine and 0.30% arsenic. It is further seen from these figures that the values of S and ξ show a decrease and increase respectively in their behaviour as the concentration of dopants increases beyond the above mentioned optimum levels. Also, it is interesting to note that there is a considerable reduction in the values ξ from the values reported [1] earlier in combinationally doped films having chlorine and arsenic concentrations of 10-20 ppm and 0.35% respectively. In fact, ξ decreases from a value of 30-40 eV per pair in the previously reported value to a value as low as ~21 eV per pair in the present case. This reduction in the value of ξ may be attributed to the enhancement in the doping levels of chlorine, i.e. from a value of 10-20 ppm in the earlier studies to a value of \sim 30 ppm in the present case. Because chlorine, when doped in a-Se, is known [10, 11] to enhance the rate of generation of holes by way of its electronegativity, it diffuses into the amorphous/crystalline regions of selenium, thus introducing [4, 11, 13, 14] conducting paths at these grain boundaries which reduce the barrier existing at these grains which results, ultimately, in the enhancement in the mobility of charge carriers and their transportation in the material. This suggested mechanism of chlorine doping finds further support from other recent investigations [15] made on xerographic effects of chlorine additions to a-Se. In these investigations [15] it was found that chlorine decreased the acceptance potential of a-Se, increased its dark decay and decreased the residual potential; this was attributed to the decrease in the release time of the holes, in other words the increase in their rate of generation. This is a similar mechanism to that suggested above based on the present investigations. Similarly, arsenic is known [10, 11] to play a complementary role in a-Se to that of chlorine as explained above, and it sustains [5, 8, 16] the dark resistivity of the material and allows it to accept more potential, thus increasing the electric field existing across the film at the time of x-ray exposure and hence ultimately resulting in the enhancement in the mobility and transportation of charge carriers by reducing the possibility of their recombination. However, it is interesting to note that this complementary, yet supportive, role of the two dopants towards enhancing the sensitivity of a-Se remains only up to a certain optimum level of doping of these two dopants, which have been found by these investigations to be \sim 30 ppm chlorine and ~30% arsenic. Beyond these optimum levels, as seen from figures 2 and 3, the values of S and ξ show a reverse trend. This reverse trend may perhaps be attributed to the excessive accumulation or formation of ionic/molecular aggregates at high doping levels, known to reduce the conductivity of the material rather than enhancing it as has been observed [17] in other amorphous materials such as polymers.

4. Conclusion

In conclusion, it is suggested that the maximum x-ray sensitivity in a-Se is achievable at optimum doping levels, i.e. ~ 30 ppm chlorine and $\sim 0.30\%$ arsenic, which gives the maximum value of S as ~ 15.5 R⁻¹ and the minimum value of ξ as ~ 21 eV per pair respectively and which has been attributed to the optimum combinational and complementary roles played by the two dopants in enhancing the mobility of charge carriers through different mechanisms as explained above.

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